DEQ
Montana Department of Environmental Quality

Quality Assurance Project Plan:

Canyon Ferry Lake Numeric Nutrient Criteria Development using a Computer Water Quality Model

April 2015

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ACRONYM LIST (WILL NEED UPDATE-CARRIE)

Acronym	Definition
DEQ	DEQ of Environmental Quality (Montana)
EDD	Electronic Data Deliverable
EPA	Environmental Protection Agency (US)
HDPE	High-Density Polyethylene
LCS	Laboratory Control Samples
LQAP	Laboratory Quality Assurance Plan
MAS	Monitoring and Assessment Section
MS	Matrix Spikes
MSA	Method of Standard Additions
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RPD	Relative Percent Difference
SAP	Sampling and Analysis Plan
STORET	EPA STOrage and RETrieval database
SVF	Site Visit Form
TDS	Total Dissolved Solids
TMDL	Total Maximum Daily Load
TN	Total Nitrogen
TOC	Total Organic Carbon
TP	Total Phosphorus
TSS	Total Suspended Solids
USGS	United States Geological Survey
WQPB	Water Quality Planning Bureau (DEQ)

1.0 PROJECT TASK/ORGANIZATION

This document presents the quality assurance project plan (QAPP) and Sampling Plan for the development of numeric nutrient criteria for Canyon Ferry Lake using a water quality model. Quality assurance descriptions for both field data collection as well as model development are provided herein. Field data collection activities will be completed as part of a cooperative effort between the Montana Department of Environmental Quality (MT DEQ), U.S. Geological Survey (USGS), and the U.S. Environmental Protection Agency (EPA). Model development will be completed solely by MT DEQ. Laboratory analysis will be done by the Montana Department of Public Health and Human Services (DPHHS) Environmental Laboratory, USGS National Water Quality Laboratory (NWQL), Agricultural Analytical Services Lab at Penn State University, and the Denver EPA Laboratory. Biological samples will be identified by the Academy of Sciences at Drexel University and by Rhithron, Inc. in Missoula, MT. Rosie Sada, Michael Suplee and Kyle Flynn will provide overall project oversight for this study. The following chart shows the roles of the various entities and their relationship to one another (**Figure 1-1**).

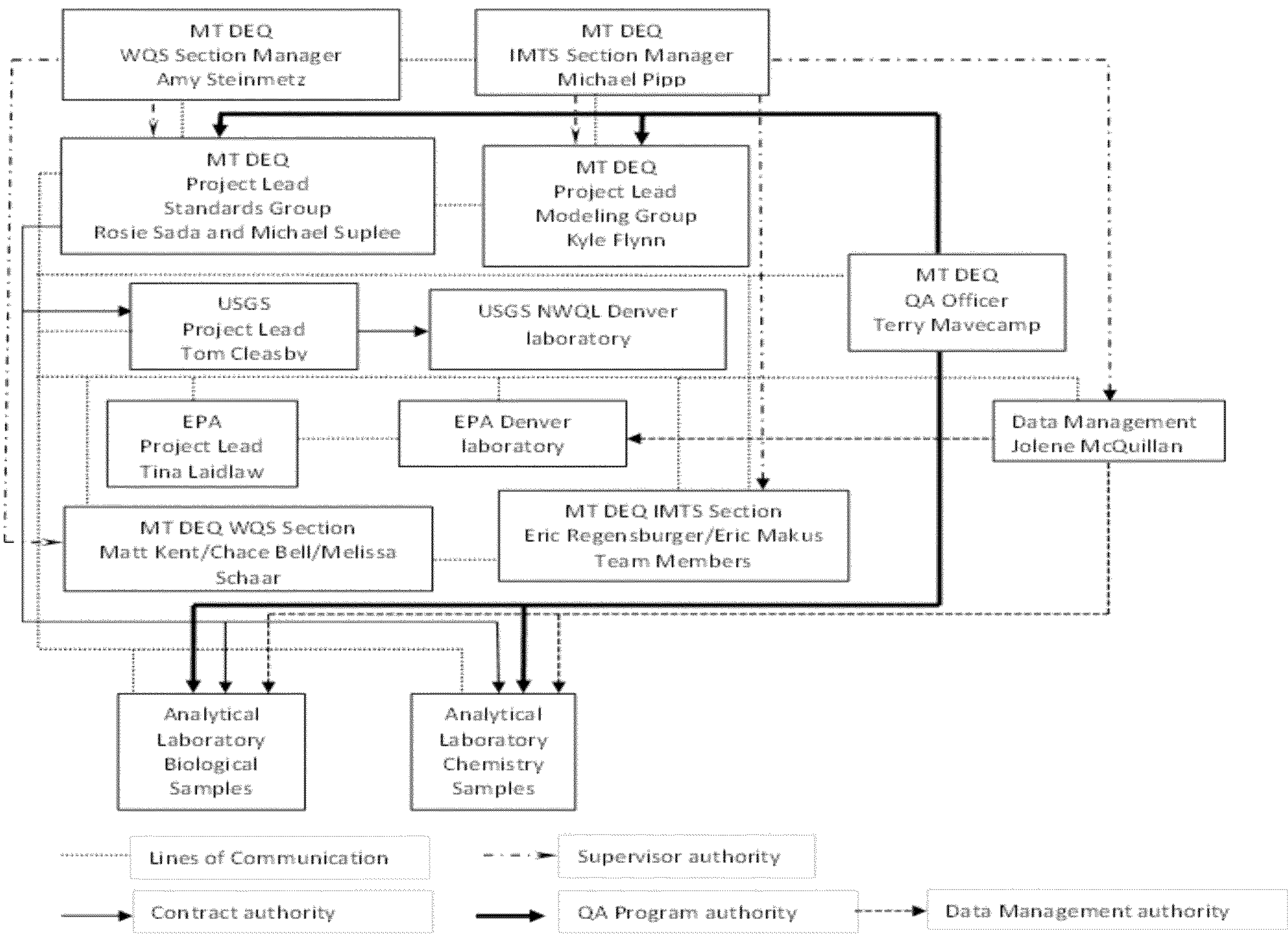

Figure 1-1. Project Organization Chart.

2017-010046-0000276

2.0 Problem Definition/Background

Canyon Ferry is a dimictic eutrophic to hyper-eutrophic lake formed from an impoundment of the Upper Missouri River with a 40.2 km length, a maximum width of 7.2 km, and a maximum depth of 50 m. The Missouri River contributes almost all water and nutrient input to the lake. Discharge through the dam is primarily through the penstocks at elevation 1,130 m. Water is also withdrawn at 1,125 m for Helena Valley Irrigation, and under high flow, either over the dam spillways or through a river outlet at 1,114 m. Mid-level withdrawals from the lake tend to reduce the eutrophication process by flushing nitrogen and phosphorus from deep levels. Canyon Ferry Lake is usually covered on ice from late November through April. The lake is used for flood control, irrigation, municipal and industrial water supply, power, and recreation (Rada, 1974; Priscu, 1987; Horn and Boehmke, 1998).

Eutrophication (i.e. over-enrichment usually from nitrogen [N] and phosphorus [P]), light intensity, and temperature have been shown to cause nuisance algal blooms and result in undesirable water-quality changes in many lakes across the world (Chorus and Bartram, 1999). These can impact beneficial uses, which in Montana include growth and propagation of fish and associated aquatic life, drinking water, agriculture, industrial supply and recreation (ARM 17.30.621 through 629). Since 2001, MT DEQ has been working to develop numeric nutrient criteria for surface waters to protect waterbodies and their associated beneficial uses from the adverse effects of eutrophication.

In Canyon Ferry Lake, algal blooms have been common since 1957 (Wright et al., 1974). Most algal blooms in this lake are caused by blue-green–algae knowns as cyanobacteria (Wright et al., 1974; Rada, 1974; Priscu, 1987; Horn and Boehmke, 1998). Cyanobacteria have a detrimental effect on water supply and recreation because of their extensive growth capacity and toxin production. Cyanobacteria have the ability to use light more efficiently and at various light spectrums than other phytoplankton because of their pigment composition and their ability to produce gas vacuoles that allows them to move vertically through the water column to find the best light growth conditions. Cyanobacteria's slow growth rate in water with long retention times favors algal bloom development as well as their ability to grow in temperatures around 25°C. Cyanobacteria can also out-compete other phytoplankton species under N or P limitation and store P very efficiently, increasing their cell division rate as well as thrive under a low N:P ratio (10-16:1 molar ratio). Furthermore, cyanobacteria can fix atmospheric nitrogen under the appropriate light conditions and can form colonies or filaments that occupy different niches in the lake from top to bottom (Chorus and Bartram, 1999).

Toxins produced by cyanobacteria might be toxic or not, and produce unpleasant odor and taste in the water. Toxin occurrence, distribution and frequency have been studied around the world since the 1980s using mouse assays, and currently via more sophisticated analytical methods such as enzyme-linked immunosorbent assays (ELISA), liquid chromatography, and mass spectrophotometry (Chorus and Bartram, 1999; Graham et al., 2008). In Canyon Ferry Lake, phytoplankton succession follows a characteristic pattern of temperate lakes. During winter and spring, phytoplankton is dominated by diatoms (chrysophyta) and small flagellates (cryptophytes), followed by diatoms, cryptophytes and cyanobacteria (cyanophyta), with some dinoflagellates (pyrrophyta) and green algae (chlorophyta) in early summer. By mid-summer and early fall, cyanobacteria are the dominant algae with different species which will tend to produce blooms under the right conditions. As soon as the water gets colder, cyanobacteria disappear and the cycle begins again with diatoms (Priscu, 1987; Horn and Boehmke, 1998).

Zooplankton are organisms that graze on the phytoplankton, their populations tend to increase in spring and decrease when cyanobacteria are dominant since they are not an adequate food source (Priscu, 1987; Horn and Boehmke, 1998). Another factor that might influence algal blooms is the amount of arsenic. A study conducted in heavily arsenic contaminated ponds demonstrated seasonal variation on phytoplankton and cyanobacteria being the dominant organism (Meeinkuirt, 2008). In Canyon Ferry Lake, arsenic concentrations are elevated (water 10.4-24.9 µg/L, sediment 5.4-14.7 mg/kg). The main sources are natural (geothermal activity in the Madison river drainage), with a likely minor component that could be human caused by using products that contain arsenic such as insecticides, herbicides, fungicides, algicides, wood preservatives and growth stimulants (Horn and Boehmke, 1998).

Although Canyon Ferry Lake has been studied in depth throughout the years, there has not been any study related to the toxins produced in the lake and what might be the most effective way to control the algal blooms that occur in the lake almost every year. We believe that a reasonable way to proceed towards the development of nutrient criteria in Canyon Ferry Lake is to identify the valued ecological attributes, determine how those clearly relate to beneficial uses, and then evaluate causal relationships (i.e. stressors and responses) between those variables via simulation modeling. The more clearly an impact threshold to a valued ecological attribute/beneficial-use can be defined, the more defensible the nutrient criteria that prevent the impact will be. Herein, we propose developing numeric nutrient criteria on Canyon Ferry Lake through a dynamic model (CE-QUAL-W2). This is a two-dimensional, longitudinal/vertical, hydro-dynamic , and water quality model applicable to relatively long and narrow waterbodies exhibiting longitudinal and vertical water quality gradients and minimal lateral variation (Cole and Wells, 2015). Because there are clear impact thresholds for the water quality state-variables listed below, we intend to model toward the following endpoints, of which the most limiting one will ultimately be used to guide criteria development, as was done by MT DEQ for the lower Yellowstone River (Flynn et al., 2015; Suplee et al., 2015):

1. Phytoplankton algae levels, which should be maintained below a nuisance or "undesirable" threshold (ARM 17.30.637(1)(e)). Concentrations of 10-15 µg chlorophyll *a* (Chl*a*) per liter are used in Colorado to protect aquatic life and recreation uses for reservoirs which are similar to Canyon Ferry (United States Environmental Protection Agency, 2012). The concentrations would be assessed as long-term medians or some similar descriptive statistic for summer concentrations. Secchi depth of < 1.0 m for more than 7 days per summer is another candidate endpoint based on Colorado reservoirs (United States Environmental Protection Agency, 2012).
2. Frequency of algal blooms
    a. Severe blooms in excess of 30 µg Chl*a*/L should be held to > 1 per summer (United States Environmental Protection Agency, 2012).
    b. Toxins characterization: Draft EPA health advisory (May 6, 2015; contact daguillard.robert@epa.gov) on microcystin concentrations is 1.6 µg/L for adults and 0.3 µg/L for children.
    c. Taste and odor reduction due to taste and odor forming algae will accompany reduction of Chl*a* and bloom frequency.
3. Phytoplankton successional pattern
4. Other potentially water quality limiting factors including DO in the hypolimnion, and pH excursions in the epilimnion.

The endpoints listed above will be reviewed and refined as more is learned about Canyon Ferry's specifics and updated mycrocystin recommendations are provided by EPA. This may include different criteria for regions of the lake.

Development of numeric nutrient criteria for Canyon Ferry Lake is not a guarantee that such criteria can be readily achieved. The lake's watershed is enormous and there are many nutrient sources, but most control measures would be achieved via nonpoint-source BMPs. To ask large numbers of producers to implement expensive BMPs without first having sound scientific criteria for the lake could be a waste of enormous private-sector dollars, and may not achieve the end goal. Once scientifically-sound criteria for Canyon Ferry are developed, a reasonable estimate of achievable load reductions (using off-the-shelf BMP loading coefficients) could be undertaken cost effectively. If this shows that the load reductions necessary are far away from those necessary to achieve the criteria, MT DEQ would probably not proceed with numeric criteria adoption. If the results were borderline, more sophisticated (and costly) watershed modeling could be undertaken. Depending on the results of the more sophisticated modeling, criteria adoption may or may not proceed.

3.0 Project Task/Description

3.1 Primary Question, Objective and Canyon Ferry lake Description

The project outlined in this QAPP is designed to answer the following main question:

> *In Canyon Ferry Lake, what are the highest concentrations of phosphorus and nitrogen that will not cause algal blooms to reach nuisance levels?*

Please see the bulleted endpoints in **Section 2.0** for details on what constitutes nuisance. Three sites (**Figure 3-1**) in Canyon Ferry Lake, representing the physical, chemical and biological conditions will be used as permanent sampling stations for this project. These sites were selected based on a principal component analysis (PCA) done by Priscu (1987). A principal component analysis is a statistical technique used to emphasize variation and bring out strong patterns in a dataset with respect to the variables used in the analysis.

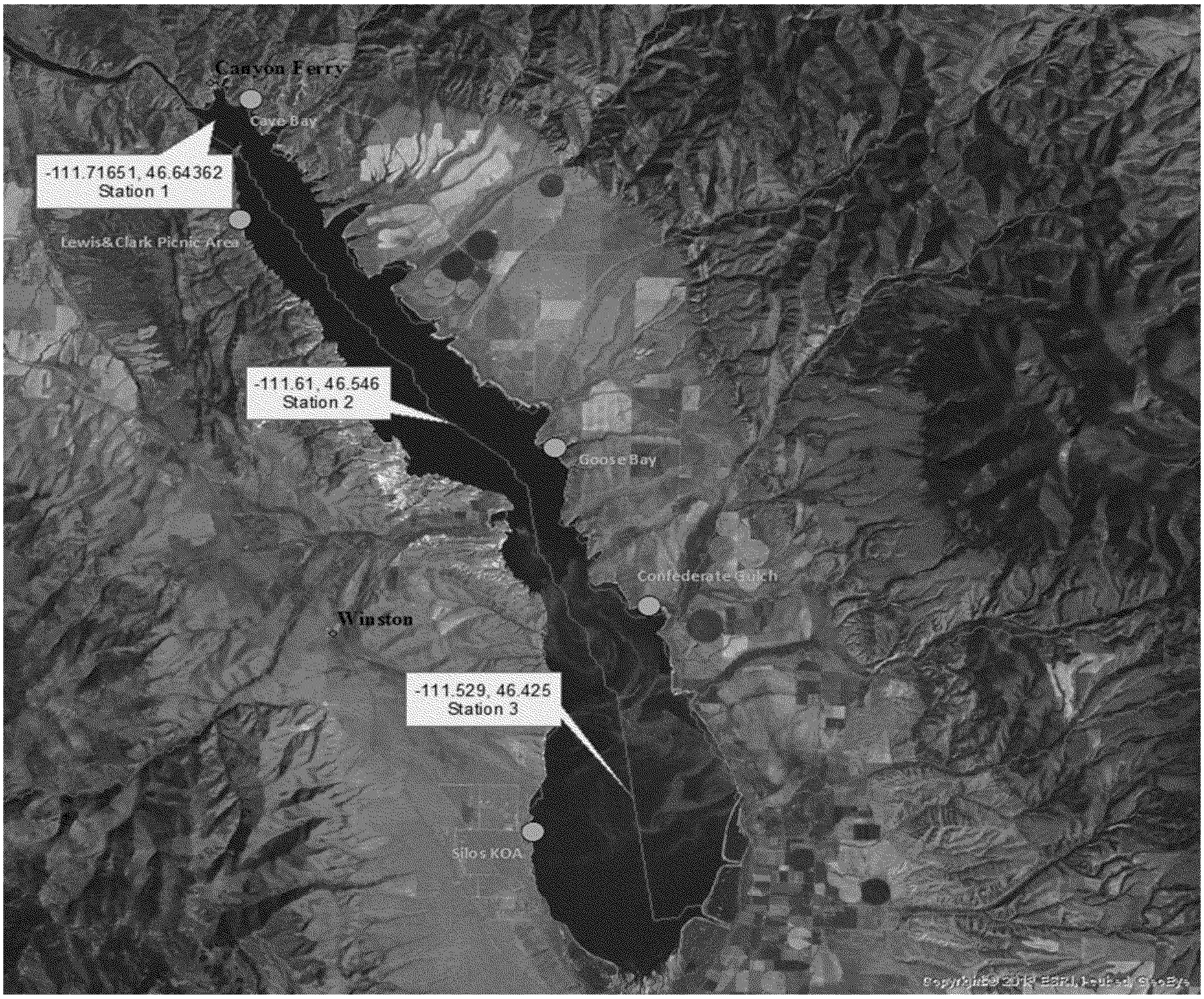

Figure 3-1. The three main sampling sites in Canyon Ferry Lake, and the proposed shoreline locations. Note the visible algae bloom in the southern end of the lake.

The intent of the model, once calibrated and validated (Cole and Wells, 2015) will be to predict changes in water quality in two dimensions (longitudinally and vertically). By calibrating and validating total and dissolved nutrients, phytoplankton chlorophyll *a* and biomass per algae groups, zooplankton populations, organic carbon, and dissolved oxygen with available measured data, the model will provide limiting thresholds to apply towards numeric nutrient criteria derivation for the lake. In order to accurately calibrate and validate the model, MT DEQ intends to measure a large number of factors that directly or indirectly influence the nutrient dynamics in the lake and that are required for the model (data will be described in subsequent sections). Our basic assumption is that direct measurement of key input forcing variables and subsequent water quality variables will increase the confidence in the model predictions and thereby reduce the uncertainty in calibrated model parameters and coefficients (Melching and Yoon, 1996; Barnwell, Jr. et al., 2004).

3.2 Project Design

3.2.1 Model Selection and Description

The main reason to select a specific model is the ability of that model to answer our proposed question in the most efficient manner. CE-QUAL-W2 is ideal, due to its ability to model the hydrodynamic (the way water moves) and the water quality behaviors of the lake. This includes predicting water surface elevations, velocities, and temperatures (the latter due to its effect on water density) as well as chemical and biological parameters that can be included in a water quality simulation. This model has been under continuous development since 1975 and has been applied to rivers, lakes, reservoirs, and estuaries. The most current Version 4.0 (alpha) includes a sediment diagenesis[1] model. The CE-QUAL-W2 model is a data intensive application. Data required for its application include bathymetric data, meteorological data (air temperature, dew point temperature, wind speed, wind direction, cloud cover, solar radiation, and precipitation), inflow and outflow volumes, inflow temperatures, evaporation, water quality constituent concentrations, and hydraulic and kinetic parameters (Bureau of Reclamation, 2009). Over 60 derived variables can be computed internally from the state variables and output for comparison to measured data. Any number of generic constituents can also be defined by a zero- or first-order decay rate, settling velocity, and Arrhenius temperature rate adjustment. The effects of salinity or total dissolved solids/salinity on density are also included. The availability and quality of these data directly affect model accuracy and usefulness. For this project, parameters absolutely necessary for the quality and accuracy of the model to answer the question on **Section 3.1** can be found in **Attachment A** (**Table 3-2** and **Section 3.2**).

3.2.2 Monitoring Program

Three sites in the lake, five shoreline sites (**Figure 3-1**) and two sites in the Missouri River (inflow and outflow) will be sampled as described in detail in **Attachment A** and **Attachment B**. The inflow site is located at USGS gages, at the Hwy 287 Bridge at Townsend, MT (06057000) and the outflow site is below Canyon Ferry Lake (06058502). Their importance and application to the overall project objectives are briefly reviewed below.

3.2.2.1 Field Water Quality Parameter Measurements

Field water quality parameters (lake profiles) are necessary for calibration of coefficients related to state variables such as temperature (T°C), dissolved oxygen (DO), pH, conductivity, phytoplankton chlorophyll *a* (phy-chl *a*), phycocyanins (phy-cya), and turbidity. A YSI 6600-V2-4 sonde will be deployed *in situ* at each site as described on Attachment A (**Sections 3.2, 3.2.1, 3.2.4**, and **6.1**) to obtain the lake profiles every month during the ice-free period. Secchi depth with the lake profile will be used to document water clarity each month as described in **Attachment A** (**Section 3.2.1**). Photosynthetic active radiation (PAR) will be collected throughout the water column at 1 meter increments using a LI-COR light sensor as described in **Attachment B**. The PAR data provides finer-scale data which can be cross-checked against the secchi depth data.

Continuous data for temperature and DO in a vertical profile is valuable for model development. To collect this data, a series of MiniDots (5) equipped with anti-fouling devices will be suspended at five

[1] Diagenesis is the sum total of processes that bring about changes in sediment or sedimentary rock (Berner, 1980). In this case, the model simulates early diagenesis, the chemical and physical changes that occur soon after a sediment is laid down.

fixed depths near the dam starting in April and will be maintained there until fall. Periodic cleaning /checking (~ monthly) of the MiniDots will occur, per recommendation in Suplee and Sada (2014).

For the riverine sites, a miniDot and a SC HOBO will be deployed from May through November of each year at the inflow and outflow sites for continuous data logger measurements of DO, temperature, and SC every 15 minutes as described in **Attachment A** (**Sections 3.4, 6.2** and **6.3**).

3.2.2.2 Water Quality Sampling

A number of water quality parameters with their sampling methods, locations, containers to be used, preservation, and sample recipients can be found in **Attachment A** (**Table 3-2** - lake sites and **Table 3-3** - inflow and outflow sites). These parameters include the physical parameters mentioned above, nutrients (total and dissolved), suspended, dissolved and volatile sediment, biochemical and carbonaceous oxygen demand, detrital material expressed as total organic carbon and dissolved organic carbon, total alkalinity, cations, anions and metals necessary for the model. Biological parameters include phytoplankton and zooplankton. Measurements related to these biological components include phytoplankton pigments (chlorophyll a and phycocyanins), carbon:nitrogen:phosphorus ratios (CNP), biomass, and identification. A detailed explanation on the data collection of each group of parameters can be found in **Attachment A** (**Sections 3.2** and **3.2.3**). Tributary inputs, point source discharges, and non-point source loadings in addition to the inflow site will be estimated by MT DEQ. The sampling event will be conducted over a 5-7 day period, once a month from May through November in 2015 and from April through November in 2016. USGS will be responsible for sampling the sites in Canyon Ferry Lake and in the Missouri River, while MT DEQ will be responsible for the deployment and maintenance of the miniDots and HOBOs in the riverine sites, weather stations in Canyon Ferry Lake, and to estimate the sediment oxygen demand in the watershed lab with sediment samples collected by USGS at two sites as described in **Attachment A** (**Section 3.2.5**). Additionally, because Canyon Ferry Lake has an established problem with algal blooms producing toxins and compounds that produce an unpleasant taste and odor, samples for these parameters (geosmin, 2-methylisoborneol, and 2,4,6-Trichloroanisole) will be collected in the three main lake sites by USGS as described on **Attachment A** (**Sections 3.2.2** and **3.2.3**), and at five sites along the shoreline where occurrence of blooms is common as described in **Attachment A** (**Section 3.5**). EPA Helena office will help MT DEQ with shoreline collection.

3.2.2.3 Streamflow and Reservoir Operations

Streamflow data is necessary to define the water balance in the model. As a result, USGS will conduct streamflow measurements at the inflow and outflow sites each month as described in **Attachment A** (**Section 3.3**) and **Attachment B**. Reservoir operations will be evaluated directly from the release rates, but operational principles will be discussed with the Bureau of Reclamation (BOR) to provide a long-term system operations compendium.

3.2.2.4 Benthic Measurements

Sediment oxygen demand (SOD) will be measured to calculate the oxygen consumption originating from the sediments which is an important component of the lake DO dynamics (Bowman and Delfino, 1980). EPA indicates that *in situ* measurements of SOD are preferable to laboratory sediment-cores techniques (Mills et al., 1986); however, deployment of *in situ* chambers in Canyon Ferry Lake is impractical due to depth, necessity of divers, etc. As such, sediment cores (a good alternative) will be taken from depositional zones and incubated in the laboratory. SOD methods are directly outlined in **Attachment A** (**Section 3.2.5**).

3.2.2.5 Meteorological Measurements

Meteorological data (i.e. air temperature, wind speed, dew point, solar radiation, etc.) are required forcing data in CE-QUAL-W2. According to Troxler and Thackson (1975) and Bartholow (1989), it is possible that the meteorological data collected at airports or in towns on the hills away from a project site may not be representative of conditions at the lake. Therefore, two independent weather station units will be installed by MT DEQ as described in **Attachment A** (**Section 3.6.2**). An adjustment procedure (Raphael, 1962; Bartholow, 1989) will be based on the assumption that the rest of the study area is fairly homogenous with respect to elevation, aspect and land use.

4.0 MEASUREMENT QUALITY OBJECTIVES AND CRITERIA

To ensure the quality of the data for decision-making, the data quality indicators (DQIs) need to be defined. DQIs which include precision, accuracy, representativeness, completeness, comparability, and sensitivity are quantitative and qualitative criteria established for the data acquired within this design to assure it is of sufficient quality for its intended use. The DQIs for this project can be found in MT DEQ (Montana Department of Environmental Quality, 2005b). The minimum concentrations (required reporting limits) necessary to effectively evaluate the project data to the project objectives will be specified in this QAPP in **Section 10** (below).

5.0 TRAINING REQUIREMENTS AND CERTIFICATION

Staff relevant to this project are trained and experienced in proper sampling, field analysis, and boat safety. Training for field procedures under this QAPP performed by either USGS or EPA will be performed by project leads Sada and Suplee (**Figure 1-1**).

Laboratories analyzing samples under this QAPP are responsible for providing personnel qualified for the methods requested and adhering to their LQAP. The laboratories that MT DEQ uses for analyzing samples are either certified through the State of Montana, accredited under national programs, or their quality system is known and meets DEQ's requirements.

6.0 Data Review, Validation and Verification

Documentation of the measurements, observations, and conditions at each site monitored is critically important for a decision to be made and validated at a later date. Site Visit Forms (SVF) and field data sheets document the activities for each site visit. SVFs and field forms will be completed on-site as the sampling occurs. The Field Procedures Manual (Montana Department of Environmental Quality, 2005a) provides instruction on completing the SVF and field forms. Adherence to the Field Procedures Manual will result in all required metadata and measurements on the field forms to produce a deliverable that is compatible for Montana DEQ's MT-eWQX database.

All hardcopy and electronic information produced from the monitoring effort will be retained indefinitely at MT DEQ in the WQPB library. In addition, all monitoring data will be submitted to MT-eWQX which will be submitted to EPA's National STORET Warehouse.

6.1 Modeling Analyses - Preliminary Data Compilation and Review

Prior to data use, MT DEQ will compile all information in a usable format for modeling. The necessary QC will be completed to ensure that field monitoring efforts, as well as ancillary data sources used in the modeling effort (i.e., other agencies or existing water quality data), are suitable for modeling purposes. USGS, BOR, and NOAA data (streamflow and weather) will be downloaded from each agency's web site and assembled into individual data files. These data will be reviewed by MT DEQ for quality factors as indicated in **Section 4**. The appropriate conversions will be made, and time-series data will be generated in a format suitable for modeling (e.g., CE-QUAL-W2 operates in SI units and on a user specified time step). Additional data disaggregation may be necessary to ascribe labile and refractory speciation for organic material and nutrients, and model boundary conditions such as streamflow, loadings, and meteorology will be input in their respective time-series. Reservoir release geometry and associated information will be compiled from BOR.

6.2 Calibration and Corroboration Methods

Complete sets of meteorological, water-quality, and hydrologic data (preferably hourly) are required for initial model calibration of CE-QUAL-W2, along with model corroboration. These should be supported with accurate measurements of physical dimensions, dam outlet configuration, and operations data (Bureau of Reclamation, 2009) as described previously. Information on calibration and model corroboration are provided below. Ideally, the model will be calibrated over a period of wet, normal, or dry years to encompass an appropriate a range of water conditions (Bureau of Reclamation, 2009).

7.0 Validation and Verification Methods

Calibration has become increasingly important with the need for valid and defensible models for TMDL development and other purposes (Donigian, Jr. and Huber, 1991; Little and Williams, 1992; Wells, 2005; Flynn et al., 2015). Model calibration defines the procedures whereby the difference between the predicted and observed values of the model are brought to within an acceptable range by adjustment of uncertain (free) parameters. Ideally, this is an iterative process whereby deficiencies in the initial parameterization are reviewed in a feedback loop to reformulate and refine the calibration. General information related to model calibration criteria and validation considerations can be found in Thomann (1982); James and Burges (1982); Donigian (1982); and Wells (2005). Validation is defined as the comparison of modeled results with independently derived numerical observations from the simulated environment. The same statistical procedures identified in the model calibration will be implemented to the validation dataset.

Model validation is, in reality, an extension of the calibration process (Reckhow, 2003; Wells, 2005) and is often referred to as confirmation or corroboration. Its purpose is to assure that the calibrated model properly assesses the range of variables and conditions that are expected within the simulation. Although there are several approaches to validating a model, perhaps the most effective procedure is to use only a portion of the available record of observed values for calibration and the other for validation (Chapra, 1997). This type of split-sample calibration-validation is proposed for the Canyon Ferry Lake modeling project. Several years of data will be used in calibration and validation, and it should be noted that if the model validation does not perform sufficiently, all is not lost (Wells, 2005). Rather, efforts should be made to re-calibrate the model so that the predictions best match both data periods.

7.1 Model Acceptance Criteria

For the purpose of this QAPP (and associated modeling efforts) two tests will be utilized to define the sufficiency of the model calibration in each of the layers and segments sampled. These are relative error (RE) and root mean squared error (RMSE) (USEPA, 2009). RE is a measure of the percent difference between observed and predicted ordinates while RMSE compares the squared difference between modeled output and observations

1) $$\mathrm{RE} = 100 \times \frac{1}{n}\sum_{i=1}^{n}\left(\frac{Y_i^{sim} - Y_i^{obs}}{Y_i^{obs}}\right)$$

2) $$\mathrm{RMSE} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(Y_i^{sim} - Y_i^{obs}\right)^2}$$

where Y_i^{obs} = observed state variable, Y_i^{sim} = simulated state variable, and n = the number of observations evaluated. Suggested acceptance criteria from the literature are shown in Table 7-1.

RE is the consistent or systematic deviation of results from the "true" value (Moore and McCape, 1993) and can be a result of a number of deficiencies. These include (1) incorrect estimation of model parameters, (2) erroneous observed model input data, (3) deficiencies in model structure or forcing functions, or (4) error of numerical solution methods (Donigian, Jr. and Huber, 1991). RMSE is a commonly used objective function for water quality model calibration (Little and Williams, 1992; Chapra, 1997) that takes the average of the sum of squared differences, and then normalizes it. Thus a difference of 10 units between the predicted and observed values is one hundred times worse than a difference of 1 unit. Squaring the differences also treats both overestimates and underestimates by the model as undesirable

7.2 Model Sensitivity Analysis

Small changes in some model parameters have a large influence on model outcomes, whereas large changes in other parameters have relatively little effect. Sensitivity analysis is a technique that can greatly enhance the model calibration process (Chapra, 2003). It guides the modeler to focus the calibration on the most sensitive model parameters and allows the user to judge the relative magnitude of various model parameters on key state variables. Sensitivity is typically expressed as a normalized sensitivity coefficient (Brown and Barnwell, Jr., 1987) in which the percent change in the model input parameter is compared to the change in model output. The equation for calculating the sensitivity of a model parameter is shown below:

$\mathrm{SC} = \frac{\Delta Y_i / Y_i}{\Delta X_i / X_i}$, where ΔX_i = the change in the model input variable X_i and ΔY_i = change in the model output variable Y_i.

Sensitivity analysis is often accomplished using a one-variable-at-a-time perturbation approach (Brown and Barnwell, Jr., 1987; Chapra, 1997). A summary of the normalized sensitivity coefficient (NSC) calculated for the one-variable-at-a-time approach will be included as part of the reporting which will include the parameter modified, the range and increment of modification (e.g. ±10%), percent change in the modeling results, and the calculated NSC. The literature will also be consulted to assess modeling efforts similar in nature to ours, e.g., Arhonditsis and Brett (2004).

Research has shown that sensitivity analyses by themselves are not adequate for characterizing model uncertainty (Melching and Yoon, 1996). Reckhow (1994; 2003) and Chapra (2003) indicate uncertainty analyses should be considered a routine part of ecological modeling studies. Uncertainty stems from the lack of knowledge regarding model input parameters (Melching and Yoon, 1996) and the processes the model attempts to describe (Beard, 1994). Potential sources of uncertainty in the CE-QUAL-W2 model include (1) estimation of uncertain model parameters, (2) uncertainty in observed model input data, (3) deficiencies in model structure and forcing functions, (4) mathematic errors in numerical methods. A basic method for assessing model uncertainty will be incorporated to approximate confidence interval for the results.

7.3 Model Usability

7.3.1 Acceptance of Modeling Results

We propose to use the 50th percentiles of performance values specified by Arhonditsis and Brett (2004) in defining model acceptance criterion, along with companion values from Thomann (1982). The acceptance of the model will be gauged by MT DEQ in several ways, including (1) review of the "goodness of fit" indices described previously, (2) comparison of simulated and observed values against *a priori* acceptance criterion. User specific criteria developed by MT DEQ for the Canyon Ferry CE-QUAL-W2 model are shown in **Table 7-1**.

Table 7-1 Preliminary Calibration and Validation Criteria for Canyon Ferry CE-QUAL-W2 model.

State-variable	Relative Error (±%)[a]	Units
Temperature	7	°C
Dissolved oxygen	12	mg/L
Nitrate	36 (25 µg/L)[b2]	µg/L
Ammonium	48 (5 µg/L)[b2]	µg/L
SRP (phosphate)	42 (2 µg/L)[b2]	µg/L
Silica	42	µg/L
Phytoplankton	44 (0.5 µg/L)[b]	µg/L
Zooplankton	70	mg/L

[a]Arhonditsis and Brett (2004), 153 aquatic modeling studies in lakes, oceans, estuaries, and rivers (50th percentile value).
[b]Thomann (1982), studies on 15 different waterbodies (rivers and estuaries). b^2 Lake Ontario only.

Model validation testing will be completed per Chapra (2003). The Level 2 approach is proposed for the Canyon Ferry Project given the fact that numeric nutrient criteria will be developed over a longer term simulation period to characterize the magnitude, duration, and frequency of water quality excursions. The credibility of these criteria will hinge on the confidence in the model predictions and the understanding of the associated sensitivity and uncertainty in model parameters.

N and P concentrations indicated by the final model as candidate criterion will be compared to the N and P concentrations found in literature values from empirical nutrient Chl*a* or secchi depth models, for example Dillon and Rigler (1974). Modeled results that differ from the comparison site/empirical models substantially, without an appropriate rationale will result in a careful re-analysis of the model input parameters. If after the re-evaluation the results from the mechanistic model still differ considerably from the other two approaches, MT DEQ will indicate this in the final report and provide discussion as to the likely reasons.

8.0 Sampling Methods

For a detailed explanation of sampling methods, please refer to **Attachment A**.

9.0 Sample Handling and Custody

Field crews are responsible for the integrity of the samples from the time of collection until shipment or drop-off to the MT DEQ, USGS, or EPA laboratory. This responsibility includes proper preservation, labeling, sample custody documentation, and storage according to the specifications in **Attachment A**.

9.1 Sample Handling Procedures

After samples are collected and labeled according to the specifications in **Attachment A**, samples are placed in a clean cooler on ice or dry ice (as appropriate) within 6 hours of sampling. This temperature will be maintained until received by the laboratory and as specified in the preservation column in Attachment A. The laboratory will keep samples in a refrigerator maintained at a constant 4°C (or frozen) until the time of analysis, which will not exceed the holding times outlined in **Attachment A**.

MT DEQ, USGS or EPA (see **Figure 1-1**) will ship/deliver samples to the contracted laboratory as needed to meet the required holding times and temperature requirements. **Table 3-2** – lake sites and **Table 3-3** - riverine sites in Attachment A detail the standardized analytical chemistry measurements that will be used for water quality assessments and includes sample container, preservation and maximum holding time information for each sample type.

9.2 Sample Custody

Custody documentation (i.e., SVF or chain of custody) will accompany all MT DEQ samples from the field to the laboratory. Field-crew personnel will initiate custody documentation before samples are stored in the cooler and maintain the custody forms until the samples are submitted to the Project Lead (Sada). The Project Lead will sign the custody documentation and inspect the integrity of the samples and documentation during the sample receipt. Any missing information or discrepancies will be communicated to the field crew. If the samples are submitted to the Project Lead or DEQ Field Tech/Laboratory Coordinator, the samples will then be taken to the laboratory and the laboratory sample custodian will sign the custody documentation indicating that the laboratory is now the custodian of the samples. The laboratory sample custodian shall inspect the integrity of the samples and documentation during the sample receipt. Any issues or discrepancies identified by the laboratory will be communicated to the Project Lead and DEQ Field Tech/Laboratory Coordinator.

10.0 Analytical Methods

Analytical methods listed in **Table 10-1** represent standard accepted procedures. Analytical method requirements and procedures are described in the associated method documents (i.e., Standard

Methods, EPA). Required reporting limits are the minimum reporting limits that the laboratory should provide results. A number of the reporting limits are more rigorous than those in Department Circulars (e.g. Circular DEQ-12A). This is because this is a project to derive nutrient standards so the lowest possible reporting limits are required.

Table 10.1.Analytical Methods and Required Reporting Limits

Parameter	*Required Method MT DEQ*	*MT DEQ RRL (µg/L)*	*NWQL laboratory LRL (µg/L)*
Total Phosphorus (TP)	EPA 365.1	1	4
Total Persulfate Nitrogen (TN)	A4500-N-C	10	50
Nitrate + Nitrite as N	EPA 353.2	5	10
Dissolved Orthophosphate	EPA 365.1	1	4
Total Ammonia as N	EPA 350.1	5	10
Total Suspended Solids (TSS) -USGS is solids residue	A2540 D	4000	15,000
Volatile Suspended Solids (VSS)	A2540 E	4000	10,000
Total Dissolved Solids (TDS)	A2540 C	4000	20,000
Biochemical Oxygen Demand	A5210 B	2000	10,000
Carbonaceous Biochemical Oxygen Demand	A5210 B	2000	10,000
Sulfate	EPA 300.0	50	20
Chloride	EPA 300.0	50	20
Total Organic Carbon	A5310 C	500	700
Dissolved Organic Carbon	A5310 B	500	230
Alkalinity (Bicarb., Carb.)	A2320 B	1000	500
Total Recoverable Iron	EPA 200.7	20	4.6
Dissolved Iron	EPA 200.7	20	4
Total Recoverable Arsenic	EPA 200.8	1	0.2
Dissolved Arsenic	EPA 200.8	1	0.1
TR Manganese	EPA 200.7	2	0.2
Dissolved Manganese	EPA 200.7	2	0.2
Total Silica	EPA 200.7	NA	18
Dissolved Silica	EPA 200.7	NA	18
Total Sulfide	A4500-S2 D	1000	1000
Dissolved Sulfide	A4500-S2 B	1000	1000
Phytoplankton Chlorophyll a	A10200H	NA	NA
Phytoplankton Ash Free Dry Weight	A10300 C(5)	NA	NA
Phytoplankton CNP	NA	NA	NA
Phytoplankton (mg/L) & ID	NA	NA	NA
Zooplankton (mg/L) & ID	NA	NA	NA
Cyanotoxins (microcystin)	ELISA	NA	NA
2-Methylisoborneol (MIB)	A6040 C*	0.001**	NA
Geosmin	A6040 C*	0.001**	NA
2,4,6-Trichloroanisole (TCA)	A6040 C*	0.002**	NA
Sediment Oxygen Demand (SOD)	NA	NA	NA
* State lab will use method A6040 C based on the lab instrument capability and their belief that it will provide the same results than either A6040 D (solid phase microextraction -SPME) or A6040 B (closed loop stripping analysis -CSLA)			
** RRLs are based on A6040 B results so the RRL might vary with A6040 C			

11.0 Quality Control Requirements

The data collected as part of this project are used in making decisions regarding the condition of the state's water quality. Quality Control (QC) is the system of technical activities used to assure and document the quality of the monitoring data. Examples of quality control activities include instrument calibration, field logbooks, SVFs, field and laboratory QC samples (e.g., duplicates, blanks, spikes, and laboratory control standards), training and data qualifiers. The MT DEQ follows specific procedures to ensure that the design is properly implemented.

11.1 Field Quality Control

The field quality controls for this project will consist of duplicate and blank samples (one per each sampling event). Field blanks are used to determine if the sampling and handling of the samples has introduced contamination. The field blanks will consist of laboratory-grade deionized water, transported to the field and poured into a sampling container following the same procedures specific to that sample. The blank will be prepared and preserved at the same time as samples are collected from the lake. Field blanks will be collected at a minimum frequency of 10% of the total number of monitoring sites. Field duplicate and blank samples are handled in the same way that regular samples are handled. Field duplicates and blanks will be labeled according to the labeling protocol outlined in **Attachment A**.

11.2 Laboratory Quality Control

All samples are analyzed by laboratories that have established QA programs that implement the following elements:

- Documented QA Plan and standardized procedures employed by the laboratory
- A demonstration of the laboratory's capabilities and qualifications to perform analytical methods
- Clear quality requirements and QC objectives for each analytical method to provide a means to evaluate the quality of the data

11.3 Data Quality Control

All analytical results received from project laboratories will be processed through the bureau's data management and QC systems prior to release to project staff for data use. This process entails receipt of EDDs from laboratories, loading the EDD into WQPB's SUDS database, applying QC review of the data, and relating the lab data with the field parameters to generate a complete data package to load into MT-eWQX. This "data package" is the combined field measurements with lab analytical results for each site visit.

The sole exception to this data handling process is for data loggers that require data download and pre-processing of the data logger record prior to that record being loaded into MT-eWQX.

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12.0 INSTRUMENT AND EQUIPMENT MAINTENANCE AND CALIBRATION

12.1 FIELD EQUIPMENT

The MT DEQ will prepare all field instruments and equipment prior to each field season by performing routine maintenance and inspection and initial calibration. Maintenance procedures are outlined in the specific instruction manuals. A maintenance logbook will be maintained by the MT DEQ Field Tech/Laboratory Coordinator for each instrument. Instruments will be calibrated prior to each field season according to the manufacturer's instructions and using approved calibration standards (National Institute of Standards and Technology traceable standards as appropriate) and buffers. Monthly calibration of YSIs will be undertaken by MT DEQ or USGS per methods detailed in **Section 6.1** of the Sampling Plan (**Attachment A**).

Continuing calibration will occur according to the frequency prescribed in specific instrument manufacturer's instructions and prior to sampling. Calibration shall be performed as often as necessary to ensure that sample readings are with the specified tolerances. Calibrations will be documented in calibration logs stored with the instrument. Corrective actions for failed calibrations are detailed in the manufacturer's instructions.

During monitoring, any field sample readings that are out of expected range are recorded on the Site Visit Form. If equipment failures are the cause of failure, equipment should be replaced immediately. The QA Officer will ensure that calibration/maintenance techniques are appropriate and will make the appropriate corrective actions.

12.2 LABORATORY EQUIPMENT

Analytical method calibration criteria are specified in the reference analytical method from EPA, APHA, or USGS. Calibrations can include initial and continuing calibrations as well as internally calibrated methods such as the Method of Standard Additions (MSA). The reporting of a result under a referenced method is a statement by the laboratory that the calibration criteria for that method have been performed, examined and pass the control limits established in the method. Results reported under a reference method without the calibrations and control limits specified in the method will not be accepted by MT DEQ.

13.0 INSPECTION AND ACCEPTANCE REQUIREMENTS FOR SUPPLIES

Before mobilization to the field, all field monitoring supplies will be inspected to ensure they are in good working condition. Calibration standards, buffers and preservatives shall be inspected to ensure they are not past the expiration date and will be discarded appropriately when expired or contamination is suspected. Extra monitoring supplies and containers will be brought into the field in the event that damage occurs.

14.0 Data Management

Data that is collected for this project will be stored in the Montana EQuIS Water Quality Exchange (MT-eWQX) database. MT-eWQX is MT DEQ's main repository for storing water-quality monitoring data, which includes physical, chemical, biological, and habitat data as well as the metadata describing the results. Metadata includes, but is not limited to, quality assurance documentation, laboratory analytical flags and other quality control flags, analytical methods, detection limits, and sampling location descriptions.

Data submitted to MT-eWQX is sent to EPA's National STORET Warehouse. MT DEQ's Information Management and Technical Services Section manages MT-eWQX and routinely uploads copies of the state's database to the national STORET database, which is maintained by the US EPA. **Figure 14-1** describes the flow of DEQ data into MT-eWQX.

14.1 Field Forms

MT DEQ uses a series of field forms to document the various field measurements and observations made by field crews. These forms are scanned so that they can be captured and uploaded to MT-eWQX.

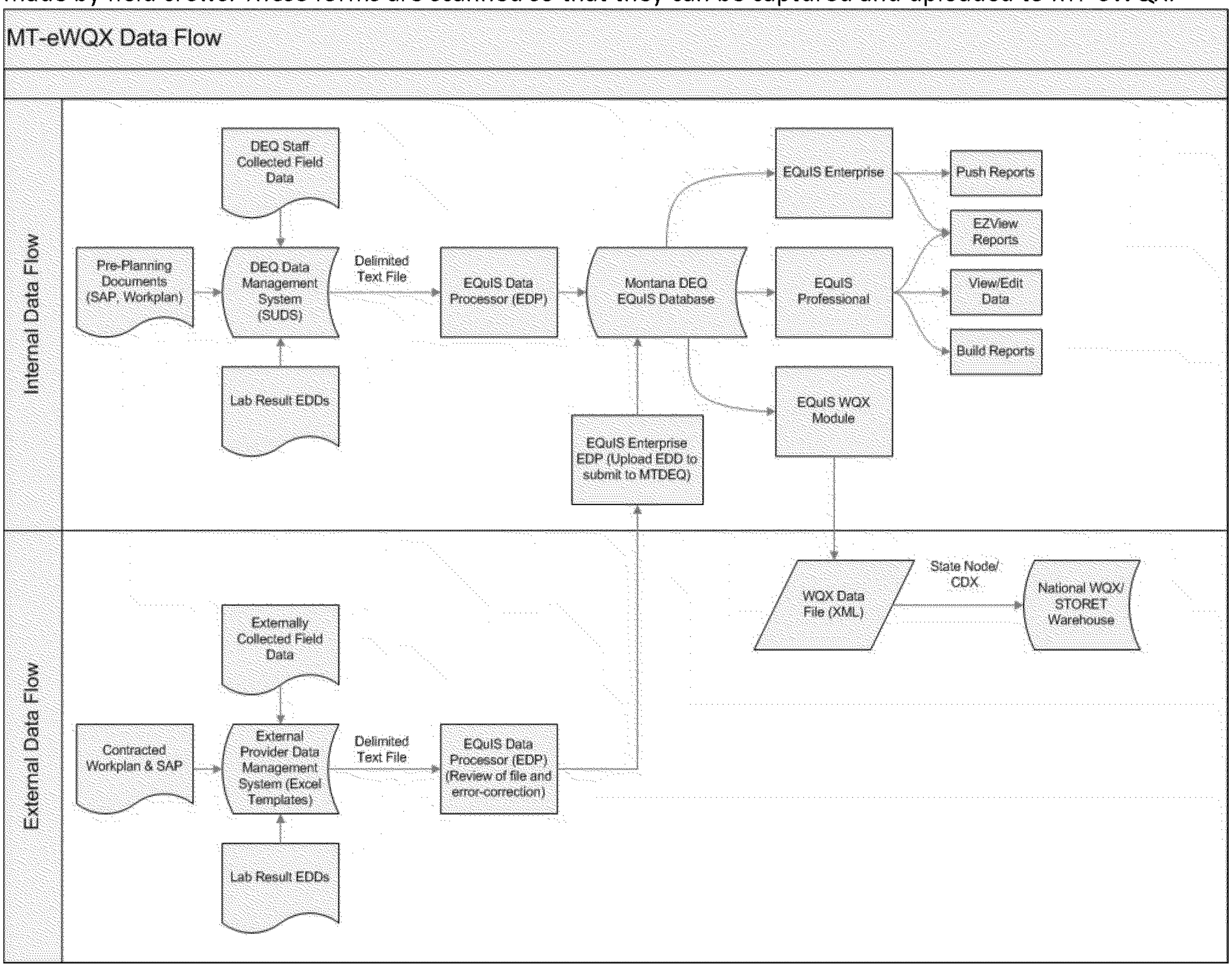

Figure 14-1. MT-EWQX Data Flow Overview.

The field forms that are used by DEQ and the instructions for completing those forms are given in the Field Procedures Manual (Montana Department of Environmental Quality, 2012) or are found in the appendices of **Attachment A**.

Field crew personnel are the first line of defense for data quality control. As such, a designated field crew member will review all field forms for completeness and accuracy. The Project Lead will then review the forms again for adequacy, calculate flow values (if applicable), and apply corrections if necessary. Once all data is entered into the database, the MT-EWQX Database Manager performs a final quality control check of the results.

14.2 Laboratory Reports and Electronic Deliverables

Analytical laboratories are required to return analytical results in a MT-EWQX specific format known as an Electronic Data Deliverable (EDD). The EDD reporting requirements can be found on the DEQ Website located at: http://deq.mt.gov/wqinfo/datamgmt/MTEWQX.mcpx. DEQ will perform the necessary validation and verification as outlined in **Section 16.0**.

15.0 Assessment & Response

All field and laboratory activities under this project are subject to an assessment by the MT DEQ QA Officer. An assessment may consist of a site visit to evaluate sample collection and/or laboratory activities or an inquest for information to support that data activities are meeting the required rigor. The MT DEQ QA Officer and Bureau Management may call for updated monitoring design as needed to maintain consistency of data among water quality monitoring programs.

15.1 Field Activity Assessments and Corrective Actions

The MT DEQ QA Officer may conduct field assessments of the field crews as needed to determine adherence with the training, project plans and SOPs. Results of field assessments will be reported to the Project Lead, WQS Section Supervisor, and Bureau Chief. Recommendations resulting from field assessments will be communicated to the crews at the time of the assessment and followed up with written comments summarizing the observations and findings. Any corrective actions identified by the QA Officer will be communicated and are effective immediately. Corrective actions will normally be addressed by the Project Lead. If it is determined that the quality of the data may have been compromised, a thorough review of the data will be performed, and questionable data will be flagged in the database.

If any QC issues arise in the field, it is the responsibility of the USGS or MT DEQ field crew personnel to communicate the issues to the Project Lead (and, in turn, to the QA Officer) promptly, so that corrective actions can be made. Any procedural problems will be corrected immediately based on recommendations from the QA Officer.

15.2 Laboratories and Contractors

Laboratories used by MT DEQ have been certified by external bodies with certification authority. The MT

DEQ QA Officer may review the laboratory QAPs to ensure that they meet the requirements for the project. The MT DEQ QA Officer may conduct an assessment of the laboratory as needed to ensure adherence to laboratory quality systems procedures as described in laboratory QAPs. Results of laboratory assessments will be reported to the IMTS Section Supervisor, WQS Section Supervisor, WQPB Bureau Chief, and Laboratory Manager. Recommendations resulting from laboratory assessments will be communicated to the Laboratory Manager at the time of the assessment and followed up with written comments summarizing the observations and findings. Any corrective actions identified by the MT DEQ QA Officer will be communicated and are effective immediately. Corrective actions will be addressed by the Laboratory Manager. If it is determined that the quality of the data may have been compromised by the laboratory based on assessments or during data QC review, a thorough review of the data will be performed, and questionable data will be flagged in the database.

The methods and required reporting limits for the project will be communicated to the laboratory before analysis to ensure that the laboratory can adequately provide the necessary services.

16.0 Data Review, Verification &Validation

To determine the adequacy of the data to support its use for this project, the data are analyzed by comparing the results to the original objectives. Data returned from the laboratories, including analytical reports, EDDs, and QC summaries, will be QC reviewed by the MT DEQ's data management group and quality assurance section to ensure the data is adequate for use.

All field and laboratory data is reviewed by the Project Lead, Data Management and QA staff to determine if the data meet project objectives described in this QAPP and associated Sampling Plans. Decisions to qualify or reject data are made by the QA Officer or delegated authority. Prior to submittal for MT-eWQX archiving, continuous data logger data for each deployed instrument will be reviewed after each field season and assessed and flagged *a posteriori* following protocols established in the addendum to the 2007 Yellowstone River Modeling QAPP(Suplee, 2007). Data will be flagged as follows:

FLAG CODES
R: Data rejected (same general definition in modern STORET).
DX: Deployed instrument data differed from the cross-check instrument.
II: Interference with instrument readings from material (e.g., filamentous algae) caught on YSI/MiniDOT or deployer.

16.1 Laboratory Verification

It is the responsibility of the laboratory to ensure that analytical results conform to the requirements of the methods that they perform. Methods must be reported under a reference analytical method from EPA, Standard Methods, USGS, or other recognized organization. Where a substantial modification to a recognized method is being performed, the laboratory must ensure that DEQ approves the modification and a reference must note this by including "mod" or "modified" following the method citation.

Laboratories will provide a QC summary of the results.

16.3 Verification and Validation Responsibilities

All data collected by MT DEQ undergo a series of checks to ensure that the data are of sufficient quality and conform to the project's objectives. As soon as possible after receipt of data from the laboratory, data verification and validation should occur. The QA Officer or the MT-eWQX Database Administrator is responsible for verifying that the laboratory data deliverables are complete and consistent with the requirements established in this QAPP and project SAP.

Supporting Documents that may be needed for the data verification and validation process include:
Copy of this QAPP
Copy of the Sampling Plan
Site Visit Forms and Field Forms
Data Packages from Laboratories (Analytical Report, EDD, QC Summary)
Equipment/Instrument Calibration Logs

Data will not be validated to the level of raw data unless systemic problems become evident from review of results and QC summaries. If analytical results are routinely failing to meet the data quality indicators specified in this QAPP, the QA Officer may request all raw data for a data set and perform a full data validation.
The QA Officer is responsible for resolving any data quality issues. Data that does not meet the objectives and project requirements specified in this document will be qualified and flagged accordingly. A description of the data qualifiers used by MT DEQ is specified in **Table 16-1**. Qualified data may be used, provided the uncertainties are known and understood. Any rejected data (data qualified with an "R") are considered unusable for this project. Data are considered useable once the data verification and validation process is complete and the data is successfully loaded to the EQuIS database.

Table 16-1. Data Result Qualifiers.

Result Qualifier	Result Qualifier Description
B	Detection in field blank
D	Reporting limit increased due to sample matrix
H	EPA holding time exceeded
J	Estimated: The analyte was positively identified and the associated numerical value is the approximate concentration of the analyte in the sample.
R	Rejected: The sample results are unusable due to the quality of the data generated because certain criteria were not met. The analyte may or may not be present in the sample.

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